Sulfonen door oxydatie van thiopheenderivaten

Melles, Johan Leo

VI. SUMMARY.

Although peracids oxidise thioethers to sulphones in excellent yields, up to now only few sulphones of thiophene derivatives — all highly arylated — could be prepared in this way. The sulphone of thiophene could not be obtained by oxidation; in cases where the preparation was described, the results could not be reproduced.

In this thesis the oxidation of thiophenes with various substituents (C_6H_5, CH_3, COR, CO_2R, Br, NO_2) is studied. Many of these could be oxidised to sulphones.

The ease of oxidation depends on place and nature of the substituents. It is an electrophilic reaction; the substituents affect the electron density of the sulphur, and thus the velocity of oxidation. In interpreting the results, a complication is that apparently some of the sulphones are not stable.

Presence of symmetrically placed phenyl or methyl groups makes the formation of sulphones possible. With asymmetrically placed phenyl or methyl groups, no sulphone can be isolated.

As 3,4-diphenylthiophene can be oxidised to the sulphone, the influence of various substituents introduced in this compound has been studied, e.g. of 2-nitro, 2-benzoyl, 2-carboxyl, etc. One nitro group prohibits the oxidation, as do two carboxyl groups. With one or two benzoyl groups oxidation is possible, also with one benzoyl and one carboxyl group.

The results can be explained by the mesomeric effect of these groups; they attract electrons from the nucleus and therefore diminish the electron density of the sulphur.

The behaviour of bromine-substituted thiophenes is also explained. The bromine atoms stabilise the sulphone, when formed.

The sulphone of thiophene cannot be prepared by oxidation. Prepared by elimination of hydrogen bromide from „butadienesulphonedibromide", it proved to be very unstable; in solution it dimerises quickly, losing sulphur dioxide.

Phenylated and methylated thiophene-1,1-dioxides react with maleic anhydride; intermediate compounds with a sulphonyl bridge cannot be isolated. The products are the endovinylene-cyclohexanetetracarboxylic anhydrides.

Most of the sulphones are not stable toward alkalis and amines. With 3,4-dimethylthiophene-1,1-dioxide however 1,4 addition of piperidine and other nucleophilic reagents is possible.

Many of the sulphones can be reduced to real thiophene derivatives. This result is quite unexpected, as reduction of simple sulphones is impossible.